Hypothesis

PREBIOTIC EVOLUTION: AN APPROACH TO POLYMERISATION BASED ON CRYSTAL STRUCTURES

M. VIJAYAN
Molecular Biophysics Unit, Indian Institute of Science, Bangalore - 560 012, India

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1. Introduction

Chemical evolution, which preceded biological evolution, is believed to have consisted broadly of three overlapping stages, namely, the origin of biological monomers, their polymerisation and the emergence of primitive cells. A number of experiments, conducted under simulated prebiotic conditions, have lent powerful support to the concept, developed by A. I. Oparin, J. B. S. Haldane and others, of the formation and the accumulation of the monomers in primordial oceans [1]. Thus, a plausible description of the first stage of chemical evolution exists.

The second of chemical evolution obviously led ultimately to ordered biopolymers with well-defined sequences of monomeric units. The process by which ordered polymers with highly non-random sequences and specific functions emerged is not begun to be understood even in principle. This is perhaps the least understood link in the evolutionary history of the biosphere. However, attempts are underway to elucidate the possible mechanisms of the condensation of monomers into oligomers or polymers under abiotic conditions. Several successful experiments have already been conducted for synthesising polypeptides and oligonucleotides in the presence of different types of condensing agents that might have existed on the primitive earth [2]. The suggestion, originally made by Bernal [3], regarding the possibility of the condensation of monomers absorbed to clay particles has also been verified [4]. However, the role of clay in condensation reactions is not yet clearly understood. A condition necessary for the non-enzymatic condensation of monomers is the proximity and the favourable juxtaposition of the reacting groups. The main purpose of this communication is to point out that this condition is met in many crystals involving the components of biopolymers and to suggest that prebiotic polymerisation could well have occurred in the crystalline state also.

2. Head-to-tail arrangement of monomers in crystal structures

An interesting arrangement of amino acids, very suggestive in the context of their polymerisation, exists in many crystalline complexes involving amino acids, among themselves as well as with other biomolecules, analysed recently in our laboratory. The crystal structure of a typical amino acid–amino acid complex, namely, arginine glutamate monohydrate, is given in fig.1 as an example of this arrangement [5]. The structure consists of alternating layers of arginine molecules and glutamate ions. In the arginine layer, the molecules are held together by ionic interactions and hydrogen bonds involving α-amino and α-carboxylate groups. The situation is thus analogous to that in proteins. The α-amino and the α-carboxylate groups are linked by covalent (peptide) bonds in proteins. Here, on the other hand, they are linked by non-covalent interactions. The adjacent layers of unlike molecules are connected to each other through a specific ion-pair interaction between the guanidyl group of arginine and the side chain carboxylate group of the glutamate ion, and a water bridge. The most significant feature of the structure in relation to chemical evolution is the 'head-to-tail' sequence of the arginine molecules in which the α-amino and the α-carboxylate groups are periodically brought into close proximity in a peptide-like arrangement.

Fig.2 shows the crystal structure of arginine

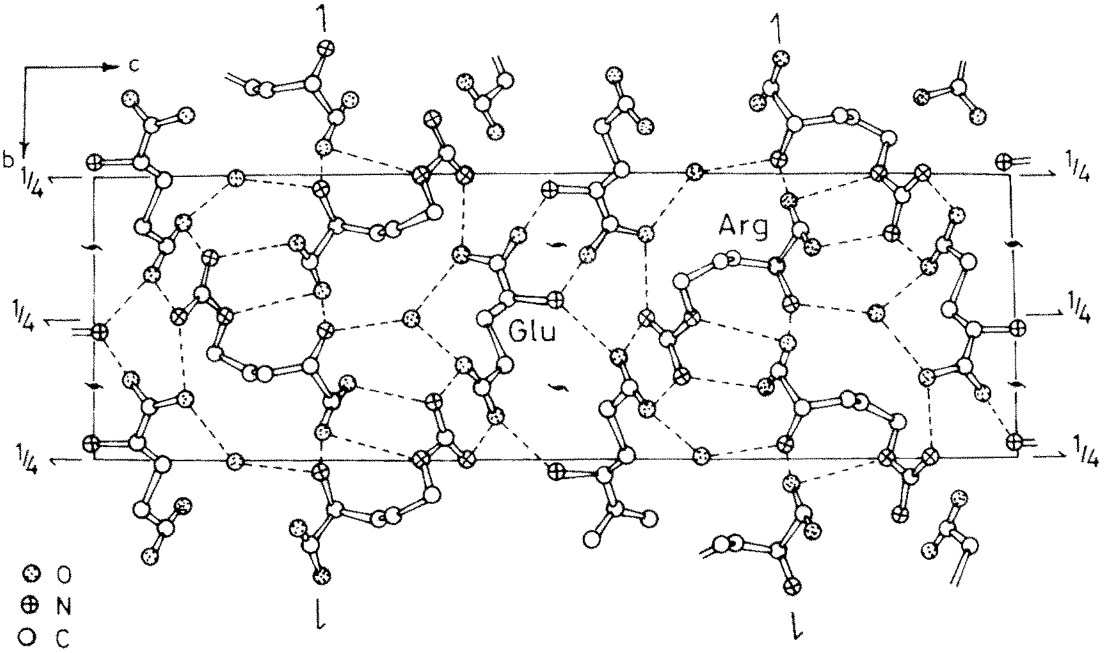

Fig.1. Crystal structure of arginine glutamate monohydrate. Hydrogen bonds are indicated by broken lines.

ascorbate, an example of a crystalline complex between an amino acid and a vitamin [6]. The unlike molecules aggregate into separate layers in this structure also. The two layers are held together principally through interactions involving the side chain guanidyl group of arginine with the ascorbate ion, a situation analogous to what might exist in the binding of ascorbate ions to proteins. Again the arginine molecules are held together in a peptide-like arrangement between α-amino and α-carboxylate groups.

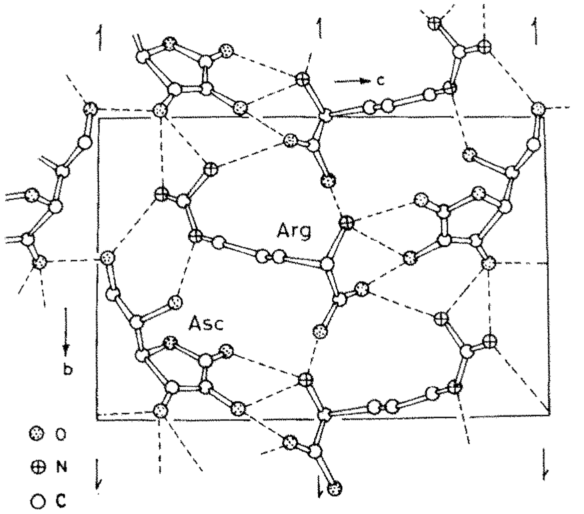

Fig.2. Crystal structure of arginine ascorbate. Hydrogen bonds are indicated by broken lines.

The characteristic head-to-tail arrangement of lysine and arginine was found, respectively, in the crystal structures of lysine aspartate [7] and arginine aspartate [8] as well. A careful examination reveals that the α-amino and the α-carboxylate groups are periodically brought into close proximity in the crystal structures of some uncomplexed amino acids also. It is equally significant to note that periodic proximity of 3′- and 5′-ends exist in some nucleotide structures as well. Thus, the chemical groups (in the monomeric units) which react through elimination of water to form biopolymers, are periodically brought into close proximity in several crystal structures.

3. Conclusion

Complexities might arise in solid state reactions as each reactive group interacts with more than one other reactive group in many of the crystal structures referred to earlier. However, in solid state reactions, it is probable that one interaction or another is preferred exclusively on the basis of energy considerations. Also, the crystal structures considered so far have arrangements appropriate to the formation of only homopolymers. Very few of the large number of possible crystalline complexes involving the components of biopolymers have been examined. The periodic head-to-tail arrangements involving more than one monomeric unit are likely to emerge when more complexes are examined.

The occurrence of crystals is as natural as that of solutions. A variety of crystallites made up of the constituents of biopolymers and their complexes are likely to have been deposited on the beaches of primordial oceans and at the bottom of lagoons due to evaporation. Abundant supplies of electrical, thermal and radiational energies are believed to have been available on the surface of the primitive earth. In this scenario, and in the light of the earlier discussion, the possibility that the favourable molecular arrangements of the monomers in the crystalline state might have been utilized merits further exploration.

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